



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup>:

C01B 7/04

A1

(11) International Publication Number:

WO 97/11026

(43) International Publication Date:

27 March 1997 (27.03.97)

(21) International Application Number: PCT/US96/15637

(22) International Filing Date: 20 September 1996 (20.09.96)

(30) Priority Data:

08/526,258

21 September 1995 (21.09.95) US

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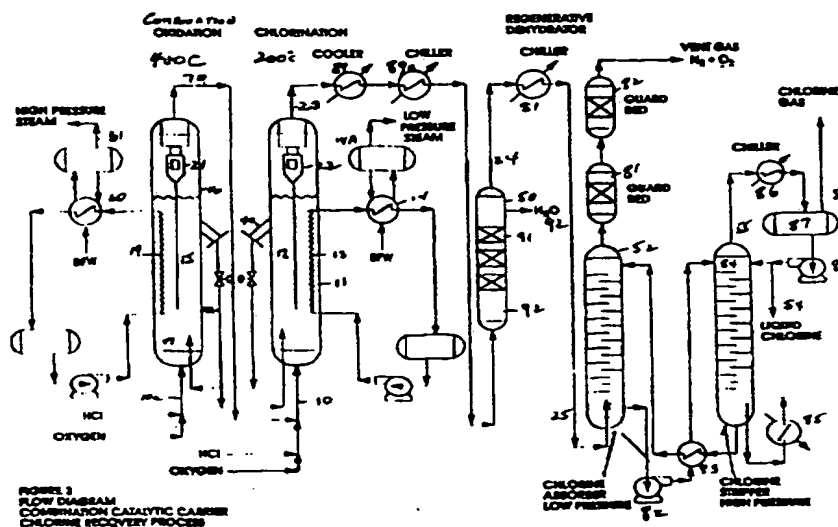
(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

## Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: EXOTHERMIC TWO-STAGE PROCESS FOR CATALYTIC OXIDATION OF HYDROGEN CHLORIDE



## (57) Abstract

A process of recovering chlorine from a stream of hydrogen chloride that includes supplying a stream HCl and oxygen to a chlorinator reactor (11) to exothermically react with a fluidized bed of carrier catalyst comprising cupric oxide and cupric chloride (15) to convert part of the cupric oxide to cupric chloride and cupric hydroxychloride; passing the carrier catalyst containing cupric chloride, cupric hydroxychloride and residual cupric oxide (40) from (11) to a combination oxidation reactor (16) to exothermically react with a stream of HCl and oxygen (10a) thereby producing cupric oxide which is returned to (11); supplying the overhead stream of chlorine, HCl, inerts and oxygen (70) from (16) to (11) to cause HCl therein to react with the cupric oxide in the carrier catalyst; the product stream (23) from (11) being chlorine rich but substantially free of HCl.

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## EXOTHERMIC TWO-STAGE PROCESS FOR CATALYTIC OXIDATION OF HYDROGEN CHLORIDE

This invention is useful in apparatus and process for the recovery of chlorine from waste or byproduct hydrogen chloride, by means of a multistage, continuous reaction exothermic process employing a combined catalytic carrier system. Hydrogen chloride is produced as a byproduct from many chemical processes, including production of titanium dioxide pigment, polyurethanes, epichlorohydrin, vinyl chloride, organic chlorides, and many other useful and economically important substances. Typically, the chlorine used in the primary chemical process is supplied from large-scale electrochemical plants by shipment via rail, truck or barge. The byproduct hydrogen chloride is usually considered to be an environmental toxic substance and must be collected and disposed of by sale at reduced price or by neutralization with some form of lime or caustic, which must be disposed of as landfill.

The herein described invention makes it possible to oxidize the hydrogen chloride to produce chlorine for recycle to the primary chemical process in an economical and environmentally sound manner, and in a two-step process carried out under exothermic conditions, to recover the chlorine for use in the primary process, thus materially reducing the quantity which must be shipped from outside, and producing useful heat, and at a cost which is significantly below the cost of fresh chlorine.

### SUMMARY OF THE INVENTION

Basically, a major object is to provide a normal process of continuously recovering chlorine from a stream of hydrogen chloride, and that includes the steps:

- a) providing at least two reactors, including an oxidation reactor and a chlorinator reactor, and providing fluidized beds of a carrier catalyst containing cupric oxide and cupric chloride in reaction zones within the reactors,
- b) supplying a stream of hydrogen chloride and oxygen to each reactor,
- c) the stream reacting in the chlorinator reactor with the fluidized bed of carrier catalyst cupric oxide and cupric chloride at temperatures between 150°

and 220°C. exothermically to convert part of the cupric oxide to cupric chloride, and cupric hydroxychloride, thereby essentially eliminating the hydrogen chloride to produce a product stream including chlorine, oxygen, inerts and water, which is removed from the chlorinator reactor, and

- 5 d) passing a stream of fluidized carrier catalyst containing cupric chloride, cupric hydroxy chloride, and residual cupric oxide from the chlorinator reactor, to be supplied to the combination reactor in a bed operating at temperatures between about 300° and 400°C, wherein the combination reactor is supplied with a stream of hydrogen chloride and oxygen to fluidize the bed, and for exothermic  
10 reaction with cupric chloride and cupric hydroxy chloride to produce cupric oxide and an overhead stream of chlorine, unrecovered hydrogen chloride, inerts, water, and residual oxygen,
- e) feeding the carrier catalyst stream containing cupric oxide to the chlorinator reactor for reaction with hydrogen chloride, as defined in c), and  
15 f) supplying the overhead stream of chlorine, hydrogen chloride, inerts, water, and oxygen from the combination reactor to the chlorinator reactor to cause hydrogen chloride therein to react with the cupric oxide in the carrier catalyst at the operating temperature between 150° and 220°C.,
- g) the product stream from the chlorinator reactor being chlorine  
20 rich but substantially free of hydrogen chloride.

Another object is to provide reactions in two steps that are carried out under exothermic conditions, thus giving a highly economic process that will not require outside fuel. The steps include recycle of catalyst of controlled composition with respect to "copper chloride", copper oxide and various copper oxy chloride  
25 complexes. Both stages are typically supplied with hydrogen chloride and oxygen.

Another object is to provide generation of heat and production of high-pressure steam in both stages, and which is in sufficient quantity to power oxygen compressors, refrigeration compressors, and produce net electric power for the overall process.

30 A further object is to provide conditions of operation that result in a chlorine product, which is free from hydrogen chloride, and which includes a secondary recovery system that separates the water without producing aqueous hydrochloric acid, by using an adsorbent regenerative dryer or an alternate liquid dehydration system with heat recovery from the two-stage process, to provide the  
35 necessary separating energy for regeneration of the dehydration agent.

An additional object is to provide another recovery step in which chlorine is separated from remaining non-condensable gas, such as nitrogen, argon, and oxygen, by the use of a specially-designed adsorbent, or liquid absorbent system. As will be seen, the overall process is low in investment cost, and less prone to corrosion, and low in operating cost, producing reclaimed chlorine at a cost significantly below the cost of fresh input chlorine.

Of importance is the fact that from an overall process point of view, the catalytic carrier chlorination step is used in a way to recycle the hydrogen chloride which appears in the combination reactor effluent, within the system, giving a product chlorine stream free from hydrogen chloride. In this regard, a major problem in a single stage catalytic oxidation process is the limit on hydrogen chloride conversion imposed by the equilibrium constraint to approximately 60% to 70% under reasonable operating conditions. By combining the single stage oxidation reactor with the catalytic carrier process as the second stage, a synergistic integration results with the off gas from the first stage being purified by the chlorination step in the second stage catalytic carrier process.

This invention improves upon the disclosure of U.S. Patent 4,959,202, and of U.S. patent application Serial No. 08/338,858, those disclosures incorporated herein by reference as background.

These and other objects and advantages of the invention, as well as the details of an illustrative embodiment, will be more fully understood from the following specification and drawings, in which:

### DRAWING DESCRIPTION

25

Fig. 1 is a block flow diagram with associated material balance listing;

Fig. 2 is a tabulation of process economic factors;

Fig. 3 is a process flow diagram;

Fig. 4 is a chlorine recovery system;

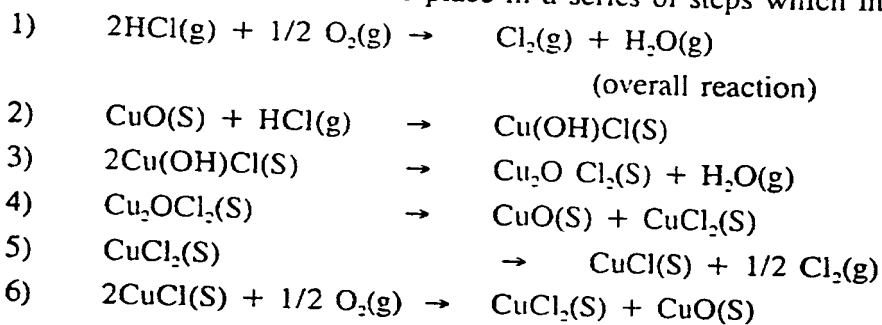
Fig. 5 is a summary of experimental data; and

Fig. 6 is a sketch of the experimental laboratory apparatus.

### Detailed Description

The process of this invention makes use of a carrier catalyst system having metallic elements in the form of complex oxides and chlorides impregnated onto a carrier mass, such as alumina, silica, zeolite, or molecular sieve material of

such a form as to be suitable for use in a multistage fluidized bed system. The chemical reactions are caused to take place in a series of steps which include:



These specific steps take place in specific reaction zones and within specific temperature ranges, as described on the block diagram, Fig. 1, and as seen in Fig. 3, and in the following steps:

Step 1. The stream 10 of oxygen, air, and of hydrogen chloride, either anhydrous or containing water and process impurities, which might be present, is passed into chlorinator reactor 11 through a fluidized bed 12 of carrier catalyst of copper oxides and copper chlorides with sodium chlorides, deposited on a suitable carrier in a 1:1 molar ratio. Reactions 2, 3, and 4 for the formation of complex chlorides take place at a temperature maintained in the range of 150° to 220°C. by providing a system 13 of heat transfer within the bed 12, which carries away the exothermic heat of reaction via, in a preferred arrangement, a heat exchanger 14 generating steam at 14a to improve the thermal economy of the process. Heat transfer fluid used at 13 and 14 is typically boiler feed water of required purity and pressure.

Chlorinated catalytic material is continuously withdrawn at 40 from the first reactor in particulate form and transferred into the fluidized bed 15 in a second reactor 16 wherein step 2 takes place.

Step 2. Stream 10a of oxygen, air and of hydrogen chloride, either anhydrous or containing water and process impurities, is passed into second, i.e., combination oxidation reactor 16 through fluidized bed 15, and the above reactions 2 through 6 take place to convert the complex chlorides to cupric oxide and cupric chloride, and release chlorine gas. The fluidized bed 15 in reactor 16 is blown with the gaseous mixture 10a of HCl and of oxygen and nitrogen ranging from 100% oxygen down to 20% oxygen entering the reactor at 17. The reactor 16 is maintained at a temperature between 300° and 400°C. by means of withdrawal of exothermically-produced heat via a system of heat transfer 19 within the fluidized

bed 15. Heat transfer occurs at 60, and steam is produced at 61. Heat transfer fluid used at 19 and 60 is typically boiler feed water of proper composition and pressure.

The gas and catalyst composition and temperature in reactor 16 result in a chemically equilibrium limited conversion by oxidation of hydrogen chloride to chlorine, leaving a significant quantity of hydrogen chloride which must be removed (see Fig. 5) to improve the overall conversion of the feed hydrogen chloride to chlorine, and to avoid contamination of the chlorine product.

The gas and catalyst composition and temperature in reactor 16 result in an equilibrium limited conversion of hydrogen chloride to chlorine leading to the presence of a certain amount of hydrogen chloride in the exit gas (see Fig. 5 table), which must be removed to improve the overall conversion of the feed hydrogen chloride to chlorine, and to avoid contamination of the chlorine product.

This removal is accomplished by step 3, the recycle at 70 of the hydrogen chloride bearing gas stream to reactor 11. A continuous stream of carrier catalyst containing cupric oxide and complex copper chlorides is withdrawn through line 41 and returned to bed 12 in the first reactor.

Step 3. The total flow of hot gas from the second reactor containing chlorine, oxygen, nitrogen, and unconverted hydrogen chloride is recycled to the first reactor 11 and the fluidized bed 12, where the contained hydrogen chloride reacts with cupric oxide returned from the second reactor 16 through 41. At the temperature conditions selected for the first fluidized bed 12, 150° to 220°C, only the hydrogen chloride reacts, the oxygen, nitrogen, water, and chlorine passing through without change. Note that reactor 12 and reactor 15 are equipped with internal dust-collecting cyclones 21 and 22, to remove catalytic dust from the exit gases and return the dust to the fluidized beds.

Step 4. Effluent gases leaving the first reactor at 23 consist of chlorine, water, oxygen, and nitrogen, which pass off to heat exchange at 89 and 89a, and to recovery system 50, for removal of water, a chiller 51, and a system for removal of chlorine at 52, and chlorine product gas at 53 and liquid chlorine at 54. When operated as described, over 99% of the hydrogen chloride 10 and 10a entering the system is recovered as chlorine product 53 and 54, gas or liquid as described in step 5.

Step 5. The gases leaving the chlorination reactor 11 pass through cooler 89 and chiller 89a to reduce the temperature level before entering the dehydrator 50, where a regenerative system utilizing multiple contact with solid

adsorbents or liquid absorbent dehydrators 91 as may be selected in a particular case. The active dehydrators remove the water from the chlorine, oxygen and nitrogen-bearing gases for later expulsion from the system 92 using a suitable means of thermal regeneration 90. Schematic diagram Fig. 4 is provided solely to illustrate  
5 a possible regenerative dehydrated system, which could use steam generated in the heat recovery portions of the main catalytic reactor system 14a.

Referring to Fig. 4, the product gas 23 from the catalytic section enters the dehydration system 50 through a valve manifold, which will direct the flow through either the dehydrator 91 or the water stripper 92 by proper positioning  
10 of automatic valves A, B, C, D, E, F, G, and H, passing through one or the other vessels in sequence. Dehydrated gas from either 91 or 92 will pass through an additional chiller 51. Water removed from the gas is retained in the multistaged adsorbent or absorbent materials until regeneration by contact with heated inert gas  
15 passed through the two vessels in sequence, to remove the water for venting and disposal.

Chilled, dehydrated gas 24 passes through the chiller 51 and enters the chlorine absorber 52 at 25 where contact with a selective solvent absorbs the chlorine in a multistage contacting system. Chlorine-free gas, consisting essentially of nitrogen and residual oxygen, passes through guard beds 81 and 82 for adsorption  
20 of trace quantities of chlorine, which is later removed. The exit gas from the guard bed may be vented to the atmosphere or recycled for utilization of the remaining oxygen if high purity oxygen has been used in the process.

From the bottom of the absorber 52, the chlorine-bearing solvent is pumped 82 through a heat exchanger 83 and delivered to a stripper 84, where  
25 chlorine is separated by raising the solvent temperature with the steam heated reboiler 85. Chlorine-free solvent flows from the bottom of the stripper and passes through heat exchanger 83 back to the chlorine absorber 52 in a continuous fashion. The chlorine 55, removed from the solvent in the stripper, flows into the chiller 86 where the partially condensed liquid is separated in the reflux drum 87 and pumped  
30 88 back to the stripper 84 with a portion of the liquid chlorine flowing to product storage 54. Uncondensed chlorine gas 53 is delivered to the product line for recycle to the original chlorine-consuming plant which generated the hydrogen chloride or for some alternate chemical use.

Since both the single stage oxidation step and the chlorination steps are  
35 exothermic, there is no need for an external source of heat, saving a significant

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quantity of fuel and capital investment. Heat available from the reactors typically produces a positive energy flow in the form of high-pressure, superheated steam, which can be used to drive compressors, and generate electric power required for pumps and other systems, making the overall operating cost attractively low.

5           As further evidence of the unique nature of this two-stage process, which was discovered during the execution of laboratory experiments, Fig. 5 is presented to illustrate the specific result of combining hydrogen chloride and oxygen as the feed stream to fluidized bed reactors containing a circulating stream of particulate materials passing between the two reactors, one of which is operating at  
10   360° to 400°C., wherein the hydrogen chloride is partially converted, as limited by chemical equilibrium, 40% to 70% by weight to chlorine, as is well known for the well-documented Deacon process, and providing for the unique new invention of passing the total effluent stream of hydrogen chloride, chlorine, residual oxygen, nitrogen, and newly-produced water vapor into a second fluidized bed reactor  
15   operating between 150° and 220°C.

          Only the hydrogen chloride reacts with the catalytic material to form cupric oxychloride and other complex copper compounds resulting in the elimination of the hydrogen chloride from the gas stream and permitting the delivery of exit gases from the low temperature reactor to a chlorine recovery system without  
20   requiring further treatment for removal of hydrogen chloride.

          The process will work in the same manner if the water vapor is removed as the gas passes between the two reactors; however, this step is not necessary for the process to operate properly.

          This discovery has been confirmed in the operation of a 4 kg/hr  
25   chlorine product pilot plant on a continuous basis. Both reactors operate in the exothermic range of the reaction leading to the generation of significant energy in the form of high-pressure steam or other suitable heat-recovery medium. Hydrogen chloride, reacting with the fluidized copper-based catalyst, to form a complex solid compound, is carried from the low-temperature reactor to the high-temperature  
30   reactor, where it is converted to chlorine. The recycle of hydrogen chloride in this manner results in the overall conversion of 100% of the feed hydrogen chloride into chlorine with a simple, two-stage exothermic system.

          The combination of these two reactors, with the circulation of catalyst between the two exothermic steps differs significantly from the process described in  
35   the recent application number 08'338,858, which makes use of a separate oxidation

reactor operating in an endothermic regime and requiring significant heat in part from an external source, and differs from U.S. Patent 4,959,202 for the same reason.

5 The experimental data given in Fig. 5 was obtained by operating a circulating fluidized bed bench scale unit, Fig. 6, equipped to analyze the inlet and outlet gases to prove the overall concept.

10 The apparatus shown in Fig. 6 consists of two 25 mm quartz reactors 300 and 301 connected with up flow transport tubes 302 and 303 for movement of the catalyst between the 400C oxidation step at 301, and the 200C chlorination step at 300. Each reactor is supplied with controlled flow of hydrogen chloride, oxygen and nitrogen. See arrows 304 and 305. The temperature is maintained at the required level by temperature-controlled electric heating tapes 306 and 307. Flow of catalyst between the reactors is moved by nitrogen injection at multiple points in the transport tubes. See 308 and 309. Exit gases from the reactors at 310 and 311 pass through dust knockout vessels 312 and 313, and to analysis for hydrogen chloride and chlorine, and pass to the vent hood for disposal. See arrows 313 and 314. Total flow rates of the order of 500 ml/min of gas enters each reactor. Solid circulation rates of 5 to 20 gms per minute are typically provided.

20 As an illustration of the economic factors for the invention, an engineering design was prepared for a plant processing 60,000 tons per year of anhydrous hydrogen chloride and an operating cost was determined based on zero value for the byproduct hydrogen chloride feed. These results, as shown in Fig. 2, indicate a chlorine recovery cost of \$78 per ton (1995 data) with a chlorine selling price of \$230 per ton on the current market.

25 Fig. 2 lists process economic factors in terms of typical plant investment and operating cost.

30 The overall system, as described, provides for 7essentially 100% conversion of hydrogen chloride to chlorine. The product chlorine can be produced as a liquid or a gas stream of 99% plus purity. No toxic or noxious effluent streams are produced to be released to the atmosphere or ground water. Energy requirements of less than 30% of the standard electrochemical process were realized, as well as significantly less than reported consumptions for alternate proposed chlorine recovery process. Fig. 1 shows material balance data.

35 As stated in the disclosure of U.S. Patent 4,959,202, the process can

be carried out using a catalytic carrier where manganese oxides and chlorides are substituted for copper, with good results, where a chlorination reactor operates with temperature in the range of 250°-350°C, and a combination reactor operates with temperature of about 400°-450°C.

5                   Iron oxides and chlorides can also be substituted.

                  Heat recovery and chlorine recovery from the product stream can be carried out as described in U.S. Patent 4,959,202.

Claims

1. In a process of recovering chlorine from a stream of hydrogen chloride, the steps that include:
  - a) providing at least two reactors, including a chlorinator reactor and a combination oxidation reactor, and providing a fluidized bed of a carrier catalyst cupric oxide and cupric chloride in a reaction zone within the chlorinator reactor,
  - b) supplying a stream of hydrogen chloride and oxygen-bearing gas to each reactor,
  - c) said stream reacting in the chlorinator reactor with said fluidized bed of carrier catalyst cupric oxide and cupric chloride at temperatures between 150° and 220°C. exothermically to convert part of the cupric oxide to cupric chloride, and cupric hydroxychloride, thereby essentially eliminating the hydrogen chloride to produce a product stream including chlorine, oxygen, inerts and water, which is removed from said chlorinator reactor, and
  - d) passing a stream of said fluidized carrier catalyst containing cupric chloride, cupric hydroxy chloride, and residual cupric oxide from said chlorinator reactor to be supplied to the combination oxidation reactor in a bed operating at temperatures between about 300° and 400°C, wherein said combination oxidation reactor is supplied with said stream of hydrogen chloride and oxygen-bearing gas, to fluidize said bed, and for exothermic reaction with cupric chloride and cupric hydroxy chloride to produce cupric oxide and an overhead stream of chlorine, unreacted hydrogen chloride, inerts and residual oxygen,
  - e) feeding said carrier catalyst stream containing cupric oxide to the chlorinator reactor for reaction with hydrogen chloride, as defined in c), and
  - f) supplying the overhead stream of chlorine, hydrogen chloride, inerts and oxygen from the combination reactor to the chlorinator reactor to cause hydrogen chloride therein to react with the cupric oxide in the carrier catalyst at the operating temperature between 150° and 220°C.,
  - g) said product stream from the chlorinator reactor being chlorine rich but substantially free of hydrogen chloride.
2. The method of claim 1 wherein heat is produced exothermically in both reactors and removed from both reactors for external use.

3. The method of claim 2 wherein heat removed from the reactors is used to produce superheated steam.

4. The method of claim 1 wherein said chlorine-rich product stream removed from the chlorinator reactor is subjected to processing for chlorine recovery, whereby at least about 99% of the chlorine content of the hydrogen chloride supplied to said reactors is recovered as to chlorine product.

5. The method of claim 1 wherein said catalytic carrier is selected from the group consisting of alumina, zeolite, silica, and molecular sieve material.

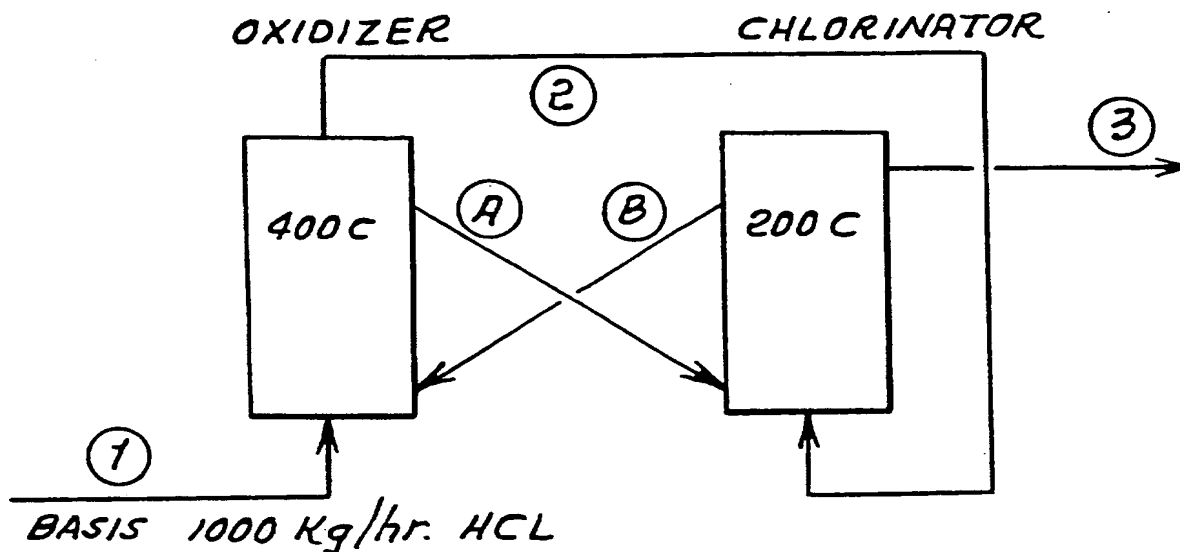
6. The method of claim 1 including transferring heat from the stream of chlorine, hydrogen chloride, inerts, and oxygen flowing from the combination oxidizer reactor to the chlorine recovery system.

7. The method of claim 1 including controlling the supply of hydrogen chloride and oxygen to the reactors.

8. The method of claim 1, including the use of cyclone separators for the removal of fine particulate matter from the fluidized beds in the reactors as the gas exits from the reactors.

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FIG. 1.



**BLOCK DIAGRAM AND MATERIAL BALANCE  
TWO-STAGE EXOTHERMIC HCL OXIDATION PROCESS**

<u>Component</u>	<u>Inlet</u> kg/hr	<u>A</u> *	<u>Outlet</u> kg/hr	<u>B</u> *	<u>Product</u> kg/hr
HCl	1000		399	399	
O <sub>2</sub>	440	220	220		220
N <sub>2</sub>	44		44		44
Cl <sub>2</sub>			974		974
H <sub>2</sub> O			246		246
	1484		1883		1484

\*Represents content of component being transferred with solid catalyst.

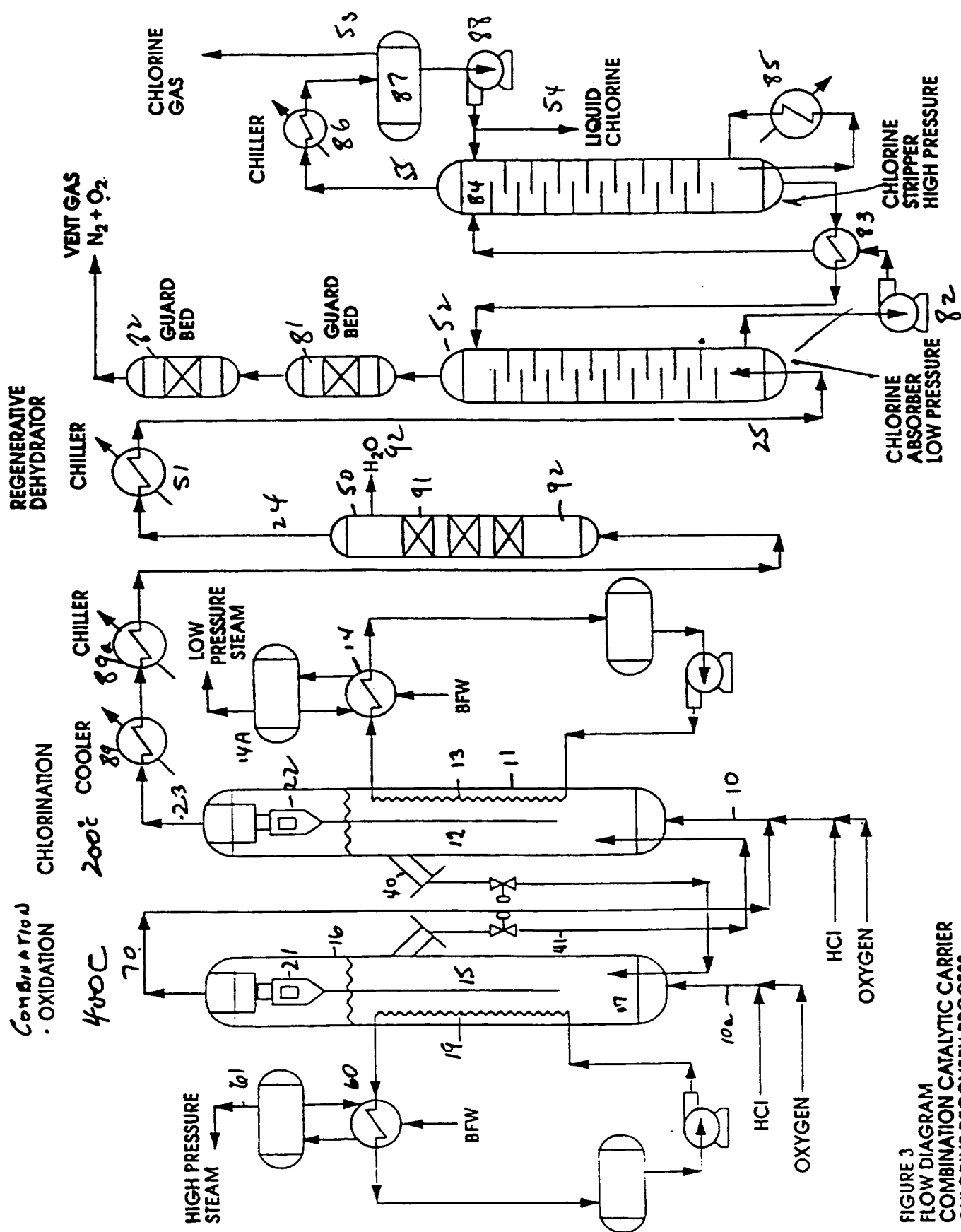
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TABLE 4

**ECONOMIC FACTORS FOR THE  
CATALYTIC OXIDATION CARRIER PROCESS****CAPACITY: 60,000 METRIC TONS PER YEAR  
OF CHLORINE PRODUCT**

<u>PLANT INVESTMENT</u>	<u>\$ MM</u>
Catalytic Carrier Section	5.0
Chlorine Recovery	2.5
Waste Heat Recovery Steam Generation	2.0
Miscellaneous	3.0
<hr/>	
Total Inside Battery Limits Cost	\$12.5
<u>OPERATING COST</u>	<u>\$/Metric Ton Cl<sub>2</sub> Product</u>
Capital Charges @ 20%	42
Utilities (Fuel, Power, Oxygen)	16
Chemicals and Catalysts	4
Labor and Overhead	6
Maintenance @ 5% Capital	10
<hr/>	
Total Cost of Production	\$78/Metric Ton

FIGURE 2



**FIGURE 3  
FLOW DIAGRAM  
COMBINATION CATALYTIC CARRIER  
CHLORINE RECOVERY PROCESS**



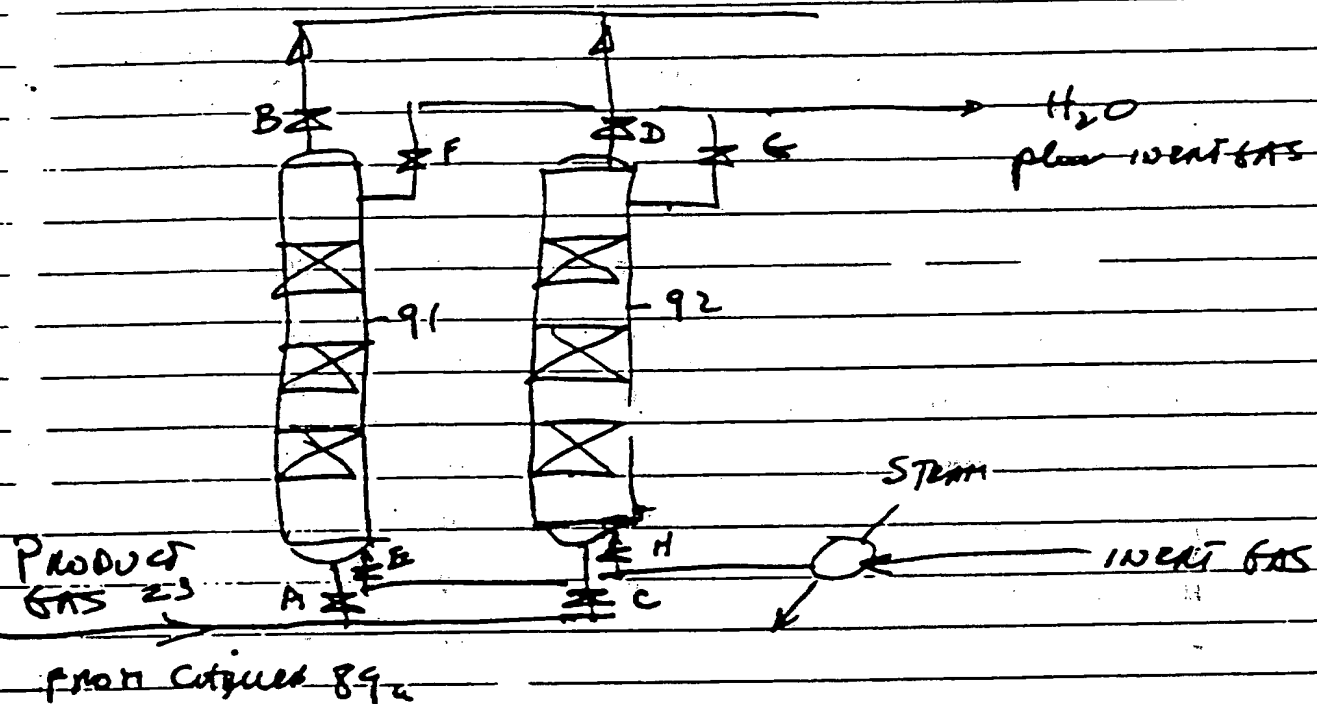


Figure 4. Schematic Regenerative Dehydrogenation System 50

TABLE 1

**CATALYTIC OXIDATION PROCESS**  
**TWO-STAGE CIRCULATING FLUIDIZED BED DATA**  
**SOLIDS CIRCULATING RATE 5-20 GMS/MIN**  
**300-400 GMS CW ON ZEOLITE CATALYST**  
**HCL OXIDATION**  
**COP MODE**

Reactor 1

<u>Reaction</u>	<u>COP</u>	<u>COP</u>	<u>COP</u>
Temperature C	200	200	200
Nitrogen flow, ml/min	450	450	450
Oxygen flow, ml/min	85	85	85
HCl flow, ml/min	70	70	70
HCl out, ml/min	0	0	0
% HCl Recovery	100	100	100

Reactor 2

Temperature C	400	400	400
Sample Time, Min	30	30	30
HCl flow, ml/min	150	150	150
Oxygen flow, ml/min	75	100	150
Nitrogen flow, ml/min	325	300	250
Chlorine out, Moles	0.11	0.12	0.12
HCl out, Moles	0.091	0.082	0.065
<hr/>			
% Chlorine Recovery	71	75	79
Total Moles of HCl	0.311	0.322	0.305
HCl Out Flow R2, ml/min	68	61	48.5

FIGURE 5

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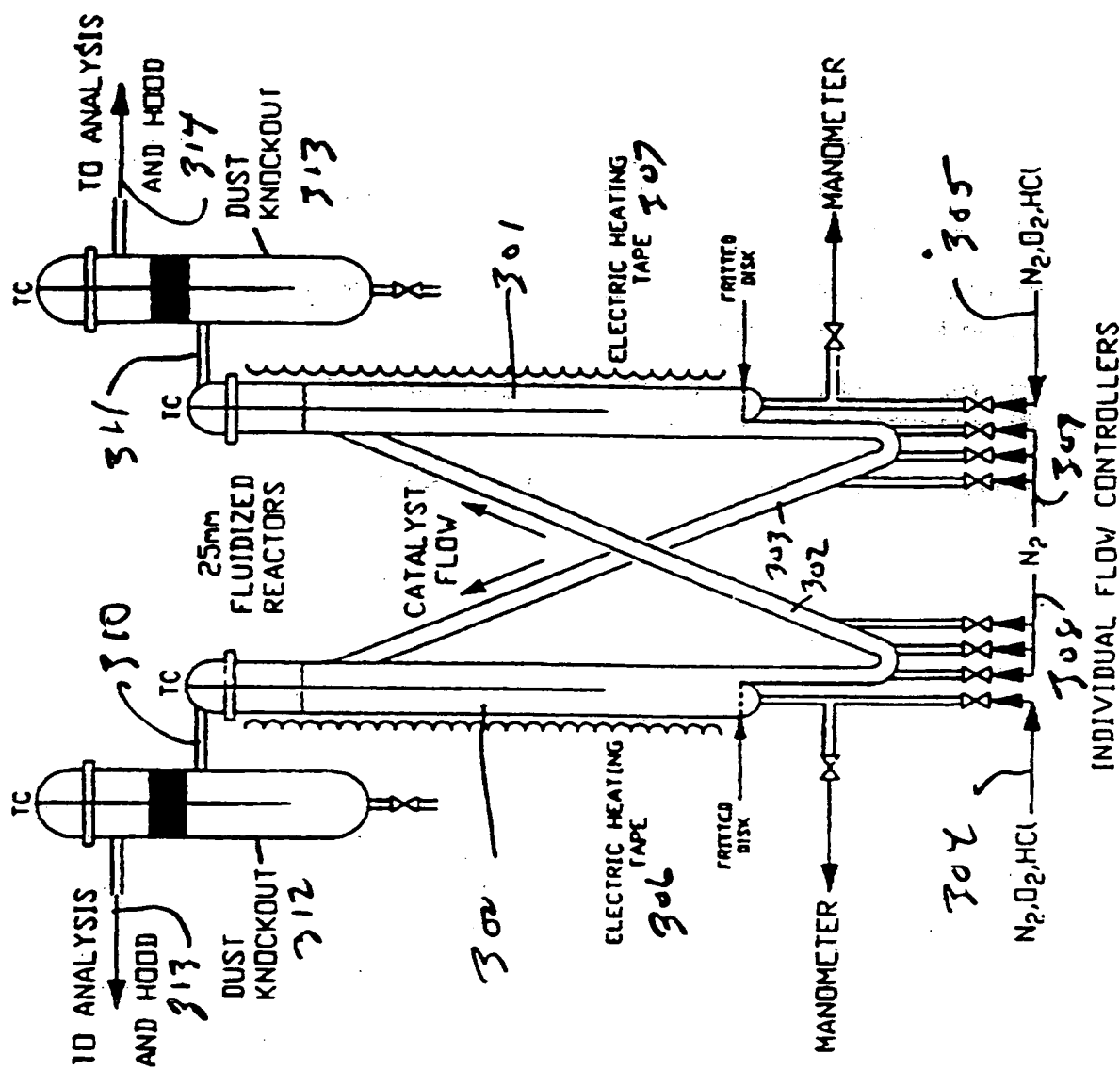


FIGURE 60 - BENCH SCALE FLUIDIZED REACTOR  
CIRCULATION RATE = 5 TO 20 GMS/MIN

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/15637

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 7/04

US CL : 423/502,507

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/502,507493,604

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
noneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
none

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,959,202 A (MINET ET AL) 25 September 1990 (25/09/90), see claim 1 and Fig. 1	
A	US 2,448,255 A (BENEDICTIS ET AL) 31 August 1948 (31/08/48), see entire document.	
A	US 4,119,705 A (RIEGEL ET AL) 10 October 1978 (10/10/78), see claim 1 and the Fig.	
A	US 3,332,742 A (METAIZEAU) 25 July 1967 (25/07/67), see entire document.	



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Date of the actual completion of the international search

23 DECEMBER 1996

Date of mailing of the international search report

04 FEB 1997

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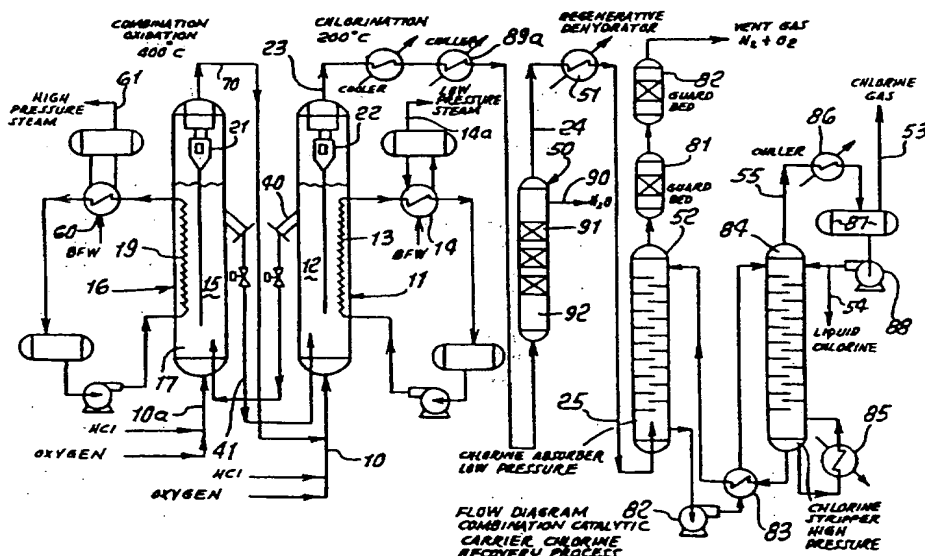
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :  C01B 7/04	A1	(11) International Publication Number: <b>WO 97/11026</b>  (43) International Publication Date: 27 March 1997 (27.03.97)
<p>(21) International Application Number: PCT/US96/15637</p> <p>(22) International Filing Date: 20 September 1996 (20.09.96)</p> <p>(30) Priority Data: 08/526,258 21 September 1995 (21.09.95) US</p> <p>(71) Applicant (for all designated States except US): UNIVERSITY OF SOUTHERN CALIFORNIA [US/US]; University Park, Los Angeles, CA 90049 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): MINET, Ronald, G. [US/US]; Apartment 310, 6140 Monteray Road, Los Angeles, CA 90042 (US). BENSON, Sidney, M. [US/US]; 110 North Bundy drive, Brentwood, CA 90049 (US). MORTENSEN, Max, K. [US/US]; 1056 Capen Avenue, Walnut, CA 91789 (US). TSOTSIS, Theodore, T. [US/US]; 16781 Phelps Lane, Hubtington Beach, CA 92649 (US).</p> <p>(74) Agent: ROTH, W., Norman; Roth &amp; Goldman, Suite 707, 523 W. 6th Street, Los Angeles, CA 90014 (US).</p>		<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>

(54) Title: EXOTHERMIC TWO-STAGE PROCESS FOR CATALYTIC OXIDATION OF HYDROGEN CHLORIDE



(57) Abstract

A process of recovering chlorine from a stream of hydrogen chloride that includes supplying a stream HCl and oxygen to a chlorinator reactor (11) to exothermically react with a fluidized bed of carrier catalyst comprising cupric oxide and cupric chloride (15) to convert part of the cupric oxide to cupric chloride and cupric hydroxychloride; passing the carrier catalyst containing cupric chloride, cupric hydroxychloride and residual cupric oxide (40) from (11) to a combination oxidation reactor (16) to exothermically react with a stream of HCl and oxygen (10a) thereby producing cupric oxide which is returned to (11); supplying the overhead stream of chlorine, HCl, inerts and oxygen (70) from (16) to (11) to cause HCl therein to react with the cupric oxide in the carrier catalyst; the product stream (23) from (11) being chlorine rich but substantially free of HCl.

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**EXOTHERMIC TWO-STAGE PROCESS FOR CATALYTIC  
OXIDATION OF HYDROGEN CHLORIDE**

This invention is useful in apparatus and process for the recovery of chlorine from waste or byproduct hydrogen chloride, by means of a multistage, continuous reaction exothermic process employing a combined catalytic carrier system. Hydrogen chloride is produced as a byproduct from many chemical processes, including production of titanium dioxide pigment, polyurethanes, epichlorohydrin, vinyl chloride, organic chlorides, and many other useful and economically important substances. Typically, the chlorine used in the primary chemical process is supplied from large-scale electrochemical plants by shipment via rail, truck or barge. The byproduct hydrogen chloride is usually considered to be an environmental toxic substance and must be collected and disposed of by sale at reduced price or by neutralization with some form of lime or caustic, which must be disposed of as landfill.

The herein described invention makes it possible to oxidize the hydrogen chloride to produce chlorine for recycle to the primary chemical process in an economical and environmentally sound manner, and in a two-step process carried out under exothermic conditions, to recover the chlorine for use in the primary process, thus materially reducing the quantity which must be shipped from outside, and producing useful heat, and at a cost which is significantly below the cost of fresh chlorine.

**SUMMARY OF THE INVENTION**

Basically, a major object is to provide a normal process of continuously recovering chlorine from a stream of hydrogen chloride, and that includes the steps:

- a) providing at least two reactors, including an oxidation reactor and a chlorinator reactor, and providing fluidized beds of a carrier catalyst containing cupric oxide and cupric chloride in reaction zones within the reactors,
- b) supplying a stream of hydrogen chloride and oxygen to each reactor,
- c) the stream reacting in the chlorinator reactor with the fluidized bed of carrier catalyst cupric oxide and cupric chloride at temperatures between 150°

and 220°C. exothermically to convert part of the cupric oxide to cupric chloride, and cupric hydroxychloride, thereby essentially eliminating the hydrogen chloride to produce a product stream including chlorine, oxygen, inerts and water, which is removed from the chlorinator reactor, and

- 5                   d)     passing a stream of fluidized carrier catalyst containing cupric chloride, cupric hydroxy chloride, and residual cupric oxide from the chlorinator reactor, to be supplied to the combination reactor in a bed operating at temperatures between about 300° and 400°C, wherein the combination reactor is supplied with a stream of hydrogen chloride and oxygen to fluidize the bed, and for exothermic  
10                   reaction with cupric chloride and cupric hydroxy chloride to produce cupric oxide and an overhead stream of chlorine, unrecovered hydrogen chloride, inerts, water, and residual oxygen,
- e)     feeding the carrier catalyst stream containing cupric oxide to the chlorinator reactor for reaction with hydrogen chloride, as defined in c), and  
15                   f)     supplying the overhead stream of chlorine, hydrogen chloride, inerts, water, and oxygen from the combination reactor to the chlorinator reactor to cause hydrogen chloride therein to react with the cupric oxide in the carrier catalyst at the operating temperature between 150° and 220°C.,
- g)     the product stream from the chlorinator reactor being chlorine  
20                   rich but substantially free of hydrogen chloride.

Another object is to provide reactions in two steps that are carried out under exothermic conditions, thus giving a highly economic process that will not require outside fuel. The steps include recycle of catalyst of controlled composition with respect to "copper chloride", copper oxide and various copper oxy chloride  
25                   complexes. Both stages are typically supplied with hydrogen chloride and oxygen.

Another object is to provide generation of heat and production of high-pressure steam in both stages, and which is in sufficient quantity to power oxygen compressors, refrigeration compressors, and produce net electric power for the overall process.

30                   A further object is to provide conditions of operation that result in a chlorine product, which is free from hydrogen chloride, and which includes a secondary recovery system that separates the water without producing aqueous hydrochloric acid, by using an adsorbent regenerative dryer or an alternate liquid dehydration system with heat recovery from the two-stage process, to provide the  
35                   necessary separating energy for regeneration of the dehydration agent.



An additional object is to provide another recovery step in which chlorine is separated from remaining non-condensable gas, such as nitrogen, argon, and oxygen, by the use of a specially-designed adsorbent, or liquid absorbent system. As will be seen, the overall process is low in investment cost, and less prone to corrosion, and low in operating cost, producing reclaimed chlorine at a cost significantly below the cost of fresh input chlorine.

Of importance is the fact that from an overall process point of view, the catalytic carrier chlorination step is used in a way to recycle the hydrogen chloride which appears in the combination reactor effluent, within the system, giving a product chlorine stream free from hydrogen chloride. In this regard, a major problem in a single stage catalytic oxidation process is the limit on hydrogen chloride conversion imposed by the equilibrium constraint to approximately 60% to 70% under reasonable operating conditions. By combining the single stage oxidation reactor with the catalytic carrier process as the second stage, a synergistic integration results with the off gas from the first stage being purified by the chlorination step in the second stage catalytic carrier process.

This invention improves upon the disclosure of U.S. Patent 4,959,202, and of U.S. patent application Serial No. 08/338,858, those disclosures incorporated herein by reference as background.

These and other objects and advantages of the invention, as well as the details of an illustrative embodiment, will be more fully understood from the following specification and drawings, in which:

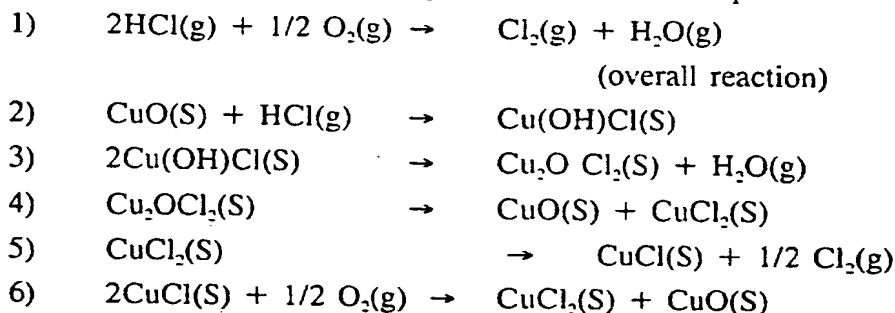
### DRAWING DESCRIPTION

- Fig. 1 is a block flow diagram with associated material balance listing;
- Fig. 2 is a tabulation of process economic factors;
- Fig. 3 is a process flow diagram;
- Fig. 4 is a chlorine recovery system;
- Fig. 5 is a summary of experimental data; and
- Fig. 6 is a sketch of the experimental laboratory apparatus.

#### Detailed Description

The process of this invention makes use of a carrier catalyst system having metallic elements in the form of complex oxides and chlorides impregnated onto a carrier mass, such as alumina, silica, zeolite, or molecular sieve material of

such a form as to be suitable for use in a multistage fluidized bed system. The chemical reactions are caused to take place in a series of steps which include:



These specific steps take place in specific reaction zones and within specific temperature ranges, as described on the block diagram, Fig. 1, and as seen in Fig. 3, and in the following steps:

Step 1. The stream 10 of oxygen, air, and of hydrogen chloride, either anhydrous or containing water and process impurities, which might be present, is passed into chlorinator reactor 11 through a fluidized bed 12 of carrier catalyst of copper oxides and copper chlorides with sodium chlorides, deposited on a suitable carrier in a 1:1 molar ratio. Reactions 2, 3, and 4 for the formation of complex chlorides take place at a temperature maintained in the range of 150° to 220°C. by providing a system 13 of heat transfer within the bed 12, which carries away the exothermic heat of reaction via, in a preferred arrangement, a heat exchanger 14 generating steam at 14a to improve the thermal economy of the process. Heat transfer fluid used at 13 and 14 is typically boiler feed water of required purity and pressure.

Chlorinated catalytic material is continuously withdrawn at 40 from the first reactor in particulate form and transferred into the fluidized bed 15 in a second reactor 16 wherein step 2 takes place.

Step 2. Stream 10a of oxygen, air and of hydrogen chloride, either anhydrous or containing water and process impurities, is passed into second, i.e., combination oxidation reactor 16 through fluidized bed 15, and the above reactions 2 through 6 take place to convert the complex chlorides to cupric oxide and cupric chloride, and release chlorine gas. The fluidized bed 15 in reactor 16 is blown with the gaseous mixture 10a of HCl and of oxygen and nitrogen ranging from 100% oxygen down to 20% oxygen entering the reactor at 17. The reactor 16 is maintained at a temperature between 300° and 400°C. by means of withdrawal of exothermically-produced heat via a system of heat transfer 19 within the fluidized

bed 15. Heat transfer occurs at 60, and steam is produced at 61. Heat transfer fluid used at 19 and 60 is typically boiler feed water of proper composition and pressure.

The gas and catalyst composition and temperature in reactor 16 result in a chemically equilibrium limited conversion by oxidation of hydrogen chloride to chlorine, leaving a significant quantity of hydrogen chloride which must be removed (see Fig. 5) to improve the overall conversion of the feed hydrogen chloride to chlorine, and to avoid contamination of the chlorine product.

The gas and catalyst composition and temperature in reactor 16 result in an equilibrium limited conversion of hydrogen chloride to chlorine leading to the presence of a certain amount of hydrogen chloride in the exit gas (see Fig. 5 table), which must be removed to improve the overall conversion of the feed hydrogen chloride to chlorine, and to avoid contamination of the chlorine product.

This removal is accomplished by step 3, the recycle at 70 of the hydrogen chloride bearing gas stream to reactor 11. A continuous stream of carrier catalyst containing cupric oxide and complex copper chlorides is withdrawn through line 41 and returned to bed 12 in the first reactor.

Step 3. The total flow of hot gas from the second reactor containing chlorine, oxygen, nitrogen, and unconverted hydrogen chloride is recycled to the first reactor 11 and the fluidized bed 12, where the contained hydrogen chloride reacts with cupric oxide returned from the second reactor 16 through 41. At the temperature conditions selected for the first fluidized bed 12, 150° to 220°C, only the hydrogen chloride reacts, the oxygen, nitrogen, water, and chlorine passing through without change. Note that reactor 12 and reactor 15 are equipped with internal dust-collecting cyclones 21 and 22, to remove catalytic dust from the exit gases and return the dust to the fluidized beds.

Step 4. Effluent gases leaving the first reactor at 23 consist of chlorine, water, oxygen, and nitrogen, which pass off to heat exchange at 89 and 89a, and to recovery system 50, for removal of water, a chiller 51, and a system for removal of chlorine at 52, and chlorine product gas at 53 and liquid chlorine at 54. When operated as described, over 99% of the hydrogen chloride 10 and 10a entering the system is recovered as chlorine product 53 and 54, gas or liquid as described in step 5.

Step 5. The gases leaving the chlorination reactor 11 pass through cooler 89 and chiller 89a to reduce the temperature level before entering the dehydrator 50, where a regenerative system utilizing multiple contact with solid

adsorbents or liquid absorbent dehydrators 91 as may be selected in a particular case. The active dehydrators remove the water from the chlorine, oxygen and nitrogen-bearing gases for later expulsion from the system 92 using a suitable means of thermal regeneration 90. Schematic diagram Fig. 4 is provided solely to illustrate  
5 a possible regenerative dehydrated system, which could use steam generated in the heat recovery portions of the main catalytic reactor system 14a.

Referring to Fig. 4, the product gas 23 from the catalytic section enters the dehydration system 50 through a valve manifold, which will direct the flow through either the dehydrator 91 or the water stripper 92 by proper positioning  
10 of automatic valves A, B, C, D, E, F, G, and H, passing through one or the other vessels in sequence. Dehydrated gas from either 91 or 92 will pass through an additional chiller 51. Water removed from the gas is retained in the multistaged adsorbent or absorbent materials until regeneration by contact with heated inert gas passed through the two vessels in sequence, to remove the water for venting and  
15 disposal.

Chilled, dehydrated gas 24 passes through the chiller 51 and enters the chlorine absorber 52 at 25 where contact with a selective solvent absorbs the chlorine in a multistage contacting system. Chlorine-free gas, consisting essentially of nitrogen and residual oxygen, passes through guard beds 81 and 82 for adsorption  
20 of trace quantities of chlorine, which is later removed. The exit gas from the guard bed may be vented to the atmosphere or recycled for utilization of the remaining oxygen if high purity oxygen has been used in the process.

From the bottom of the absorber 52, the chlorine-bearing solvent is pumped 82 through a heat exchanger 83 and delivered to a stripper 84, where  
25 chlorine is separated by raising the solvent temperature with the steam heated reboiler 85. Chlorine-free solvent flows from the bottom of the stripper and passes through heat exchanger 83 back to the chlorine absorber 52 in a continuous fashion. The chlorine 55, removed from the solvent in the stripper, flows into the chiller 86 where the partially condensed liquid is separated in the reflux drum 87 and pumped  
30 88 back to the stripper 84 with a portion of the liquid chlorine flowing to product storage 54. Uncondensed chlorine gas 53 is delivered to the product line for recycle to the original chlorine-consuming plant which generated the hydrogen chloride or for some alternate chemical use.

Since both the single stage oxidation step and the chlorination steps are  
35 exothermic, there is no need for an external source of heat, saving a significant

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quantity of fuel and capital investment. Heat available from the reactors typically produces a positive energy flow in the form of high-pressure, superheated steam, which can be used to drive compressors, and generate electric power required for pumps and other systems, making the overall operating cost attractively low.

5           As further evidence of the unique nature of this two-stage process, which was discovered during the execution of laboratory experiments, Fig. 5 is presented to illustrate the specific result of combining hydrogen chloride and oxygen as the feed stream to fluidized bed reactors containing a circulating stream of particulate materials passing between the two reactors, one of which is operating at  
10   360° to 400°C., wherein the hydrogen chloride is partially converted, as limited by chemical equilibrium, 40% to 70% by weight to chlorine, as is well known for the well-documented Deacon process, and providing for the unique new invention of passing the total effluent stream of hydrogen chloride, chlorine, residual oxygen, nitrogen, and newly-produced water vapor into a second fluidized bed reactor  
15   operating between 150° and 220°C.

          Only the hydrogen chloride reacts with the catalytic material to form cupric oxychloride and other complex copper compounds resulting in the elimination of the hydrogen chloride from the gas stream and permitting the delivery of exit gases from the low temperature reactor to a chlorine recovery system without  
20   requiring further treatment for removal of hydrogen chloride.

          The process will work in the same manner if the water vapor is removed as the gas passes between the two reactors; however, this step is not necessary for the process to operate properly.

          This discovery has been confirmed in the operation of a 4 kg/hr  
25   chlorine product pilot plant on a continuous basis. Both reactors operate in the exothermic range of the reaction leading to the generation of significant energy in the form of high-pressure steam or other suitable heat-recovery medium. Hydrogen chloride, reacting with the fluidized copper-based catalyst, to form a complex solid compound, is carried from the low-temperature reactor to the high-temperature  
30   reactor, where it is converted to chlorine. The recycle of hydrogen chloride in this manner results in the overall conversion of 100% of the feed hydrogen chloride into chlorine with a simple, two-stage exothermic system.

          The combination of these two reactors, with the circulation of catalyst between the two exothermic steps differs significantly from the process described in  
35   the recent application number 08'338,858, which makes use of a separate oxidation

reactor operating in an endothermic regime and requiring significant heat in part from an external source, and differs from U.S. Patent 4,959,202 for the same reason.

5 The experimental data given in Fig. 5 was obtained by operating a circulating fluidized bed bench scale unit, Fig. 6, equipped to analyze the inlet and outlet gases to prove the overall concept.

10 The apparatus shown in Fig. 6 consists of two 25 mm quartz reactors 300 and 301 connected with up flow transport tubes 302 and 303 for movement of the catalyst between the 400C oxidation step at 301, and the 200C chlorination step at 300. Each reactor is supplied with controlled flow of hydrogen chloride, oxygen and nitrogen. See arrows 304 and 305. The temperature is maintained at the required level by temperature-controlled electric heating tapes 306 and 307. Flow of catalyst between the reactors is moved by nitrogen injection at multiple points in  
15 the transport tubes. See 308 and 309. Exit gases from the reactors at 310 and 311 pass through dust knockout vessels 312 and 313, and to analysis for hydrogen chloride and chlorine, and pass to the vent hood for disposal. See arrows 313 and 314. Total flow rates of the order of 500 ml/min of gas enters each reactor. Solid circulation rates of 5 to 20 gms per minute are typically provided.

20 As an illustration of the economic factors for the invention, an engineering design was prepared for a plant processing 60,000 tons per year of anhydrous hydrogen chloride and an operating cost was determined based on zero value for the byproduct hydrogen chloride feed. These results, as shown in Fig. 2, indicate a chlorine recovery cost of \$78 per ton (1995 data) with a chlorine selling  
25 price of \$230 per ton on the current market.

Fig. 2 lists process economic factors in terms of typical plant investment and operating cost.

30 The overall system, as described, provides for essentially 100% conversion of hydrogen chloride to chlorine. The product chlorine can be produced as a liquid or a gas stream of 99% plus purity. No toxic or noxious effluent streams are produced to be released to the atmosphere or ground water. Energy requirements of less than 30% of the standard electrochemical process were realized, as well as significantly less than reported consumptions for alternate proposed chlorine recovery process. Fig. 1 shows material balance data.

35 As stated in the disclosure of U.S. Patent 4,959,202, the process can

be carried out using a catalytic carrier where manganese oxides and chlorides are substituted for copper, with good results, where a chlorination reactor operates with temperature in the range of 250°-350°C, and a combination reactor operates with temperature of about 400°-450°C.

5           Iron oxides and chlorides can also be substituted.

Heat recovery and chlorine recovery from the product stream can be carried out as described in U.S. Patent 4,959,202.

Claims

1. In a process of recovering chlorine from a stream of hydrogen chloride, the steps that include:

a) providing at least two reactors, including a chlorinator reactor and a combination oxidation reactor, and providing a fluidized bed of a carrier catalyst cupric oxide and cupric chloride in a reaction zone within the chlorinator reactor,

b) supplying a stream of hydrogen chloride and oxygen-bearing gas to each reactor,

c) said stream reacting in the chlorinator reactor with said fluidized bed of carrier catalyst cupric oxide and cupric chloride at temperatures between 150° and 220°C. exothermically to convert part of the cupric oxide to cupric chloride, and cupric hydroxychloride, thereby essentially eliminating the hydrogen chloride to produce a product stream including chlorine, oxygen, inerts and water, which is removed from said chlorinator reactor, and

d) passing a stream of said fluidized carrier catalyst containing cupric chloride, cupric hydroxy chloride, and residual cupric oxide from said chlorinator reactor to be supplied to the combination oxidation reactor in a bed operating at temperatures between about 300° and 400°C, wherein said combination oxidation reactor is supplied with said stream of hydrogen chloride and oxygen-bearing gas, to fluidize said bed, and for exothermic reaction with cupric chloride and cupric hydroxy chloride to produce cupric oxide and an overhead stream of chlorine, unreacted hydrogen chloride, inerts and residual oxygen,

e) feeding said carrier catalyst stream containing cupric oxide to the chlorinator reactor for reaction with hydrogen chloride, as defined in c), and

f) supplying the overhead stream of chlorine, hydrogen chloride, inerts and oxygen from the combination reactor to the chlorinator reactor to cause hydrogen chloride therein to react with the cupric oxide in the carrier catalyst at the operating temperature between 150° and 220°C.,

g) said product stream from the chlorinator reactor being chlorine rich but substantially free of hydrogen chloride.

2. The method of claim 1 wherein heat is produced exothermically in both reactors and removed from both reactors for external use.



3. The method of claim 2 wherein heat removed from the reactors is used to produce superheated steam.

4. The method of claim 1 wherein said chlorine-rich product stream removed from the chlorinator reactor is subjected to processing for chlorine recovery, whereby at least about 99% of the chlorine content of the hydrogen chloride supplied to said reactors is recovered as to chlorine product.

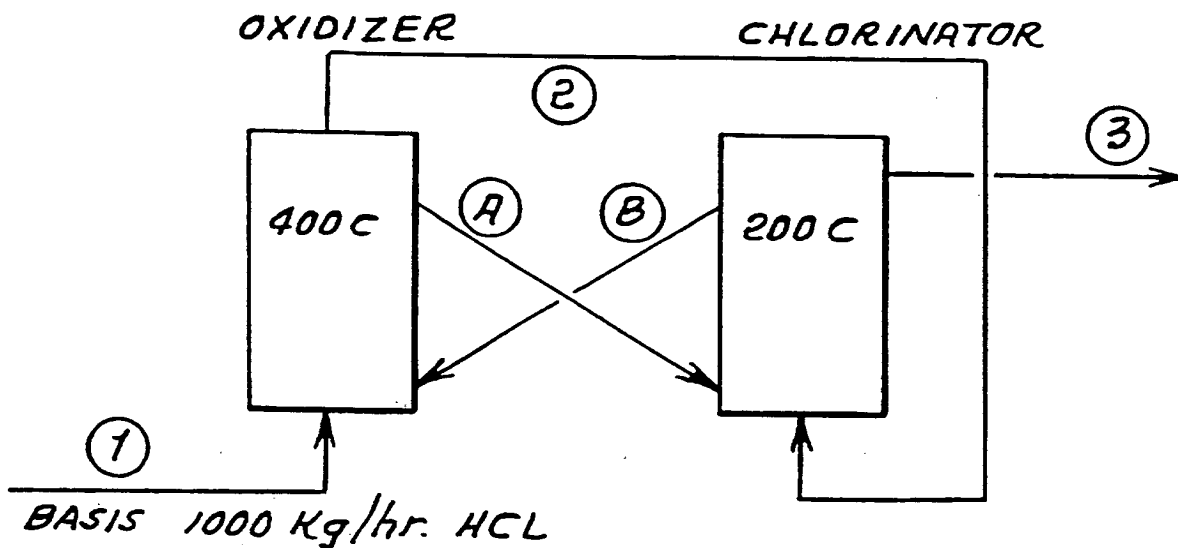
5. The method of claim 1 wherein said catalytic carrier is selected from the group consisting of alumina, zeolite, silica, and molecular sieve material.

6. The method of claim 1 including transferring heat from the stream of chlorine, hydrogen chloride, inerts, and oxygen flowing from the combination oxidizer reactor to the chlorine recovery system.

7. The method of claim 1 including controlling the supply of hydrogen chloride and oxygen to the reactors.

8. The method of claim 1, including the use of cyclone separators for the removal of fine particulate matter from the fluidized beds in the reactors as the gas exits from the reactors.

FIG. 1.



**BLOCK DIAGRAM AND MATERIAL BALANCE  
TWO-STAGE EXOTHERMIC HCL OXIDATION PROCESS**

<u>Component</u>	<u>Inlet</u> kg/hr	<u>A</u> *	<u>Outlet</u> kg/hr	<u>B</u> *	<u>Product</u> kg/hr
HCl	1000		399	399	
O <sub>2</sub>	440	220	220		220
N <sub>2</sub>	44		44		44
Cl <sub>2</sub>			974		974
H <sub>2</sub> O			246		246
	1484		1883		1484

\*Represents content of component being transferred with solid catalyst.

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*Fig. 2.*

TABLE 4

**ECONOMIC FACTORS FOR THE  
CATALYTIC OXIDATION CARRIER PROCESS****CAPACITY: 60,000 METRIC TONS PER YEAR  
OF CHLORINE PRODUCT**

<u>PLANT INVESTMENT</u>	<u>\$ MM</u>
Catalytic Carrier Section	5.0
Chlorine Recovery	2.5
Waste Heat Recovery Steam Generation	2.0
Miscellaneous	3.0
<hr/>	
Total Inside Battery Limits Cost	\$12.5
<u>OPERATING COST</u>	<u>\$/Metric Ton Cl<sub>2</sub> Product</u>
Capital Charges @ 20%	42
Utilities (Fuel, Power, Oxygen)	16
Chemicals and Catalysts	4
Labor and Overhead	6
Maintenance @ 5% Capital	10
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Total Cost of Production	\$78/Metric Ton

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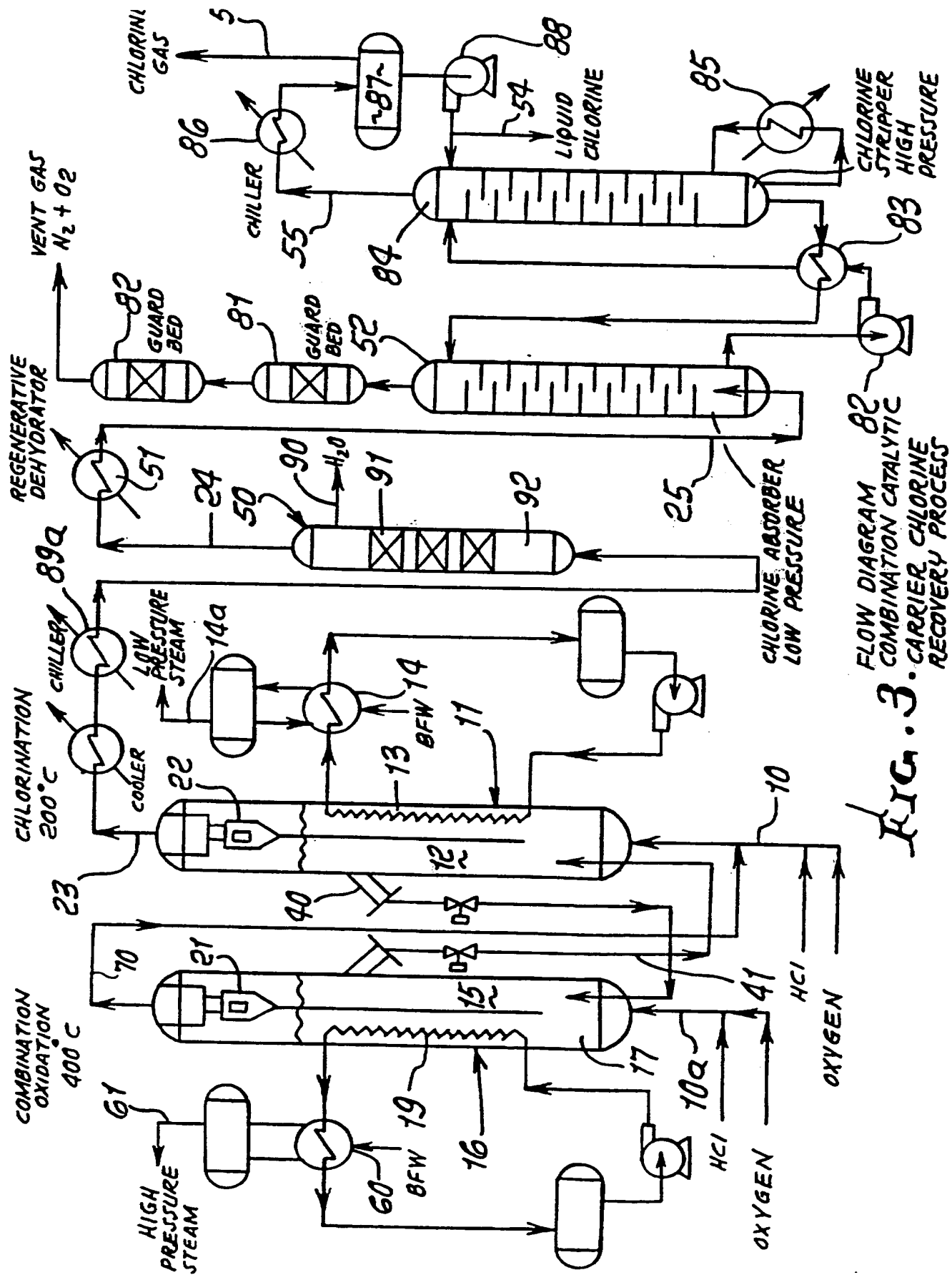
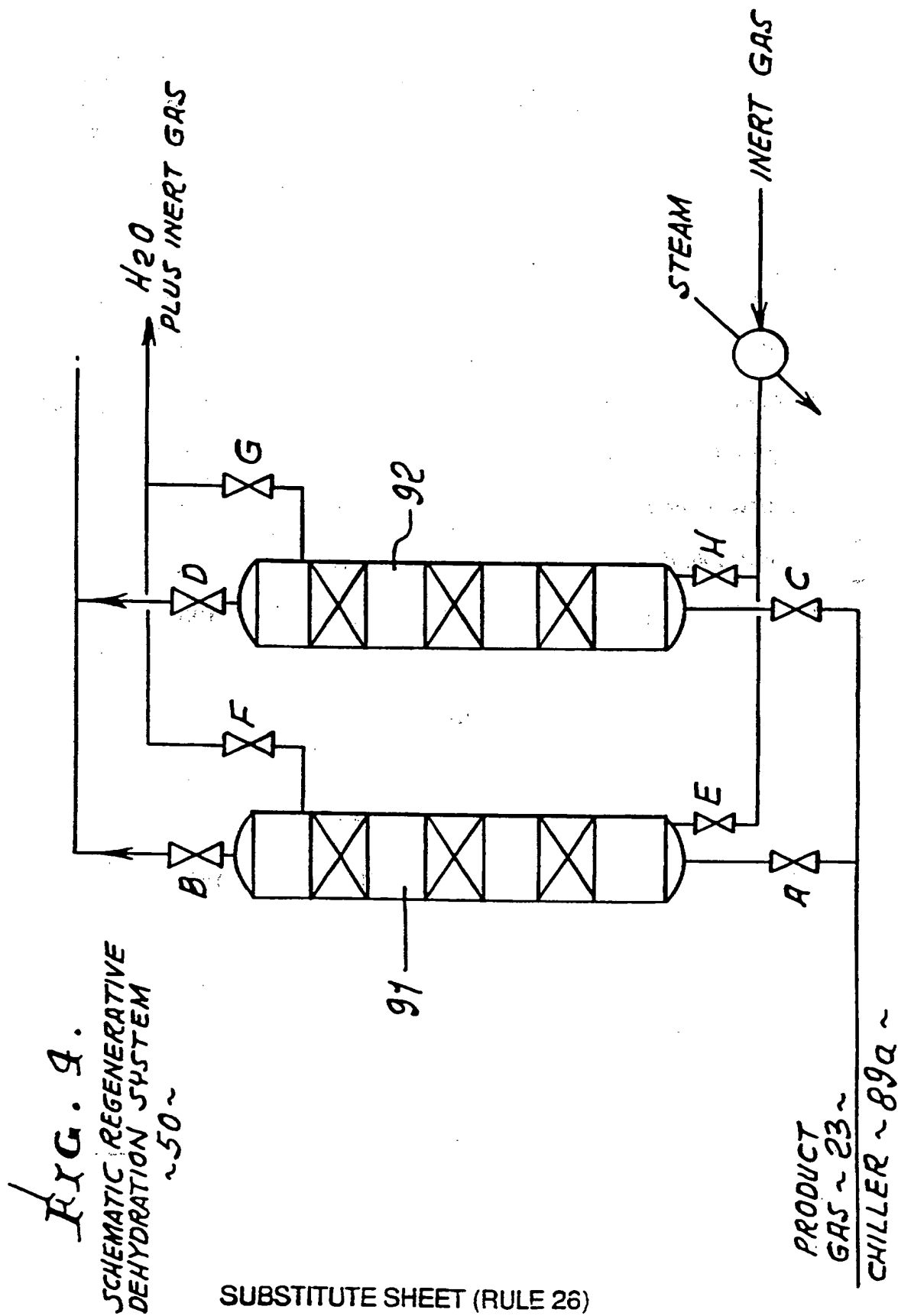


FIG. 3. FLOW DIAGRAM OF CARRIER CHLORINE COMBINATION CATALYTIC RECOVERY PROCESS

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TABLE 1

Fig. 5.

CATALYTIC OXIDATION PROCESS  
TWO-STAGE CIRCULATING FLUIDIZED BED DATA  
SOLIDS CIRCULATING RATE 5-20 GMS/MIN  
300-400 GMS CW ON ZEOLITE CATALYST  
HCL OXIDATION  
COP MODE

Reactor 1

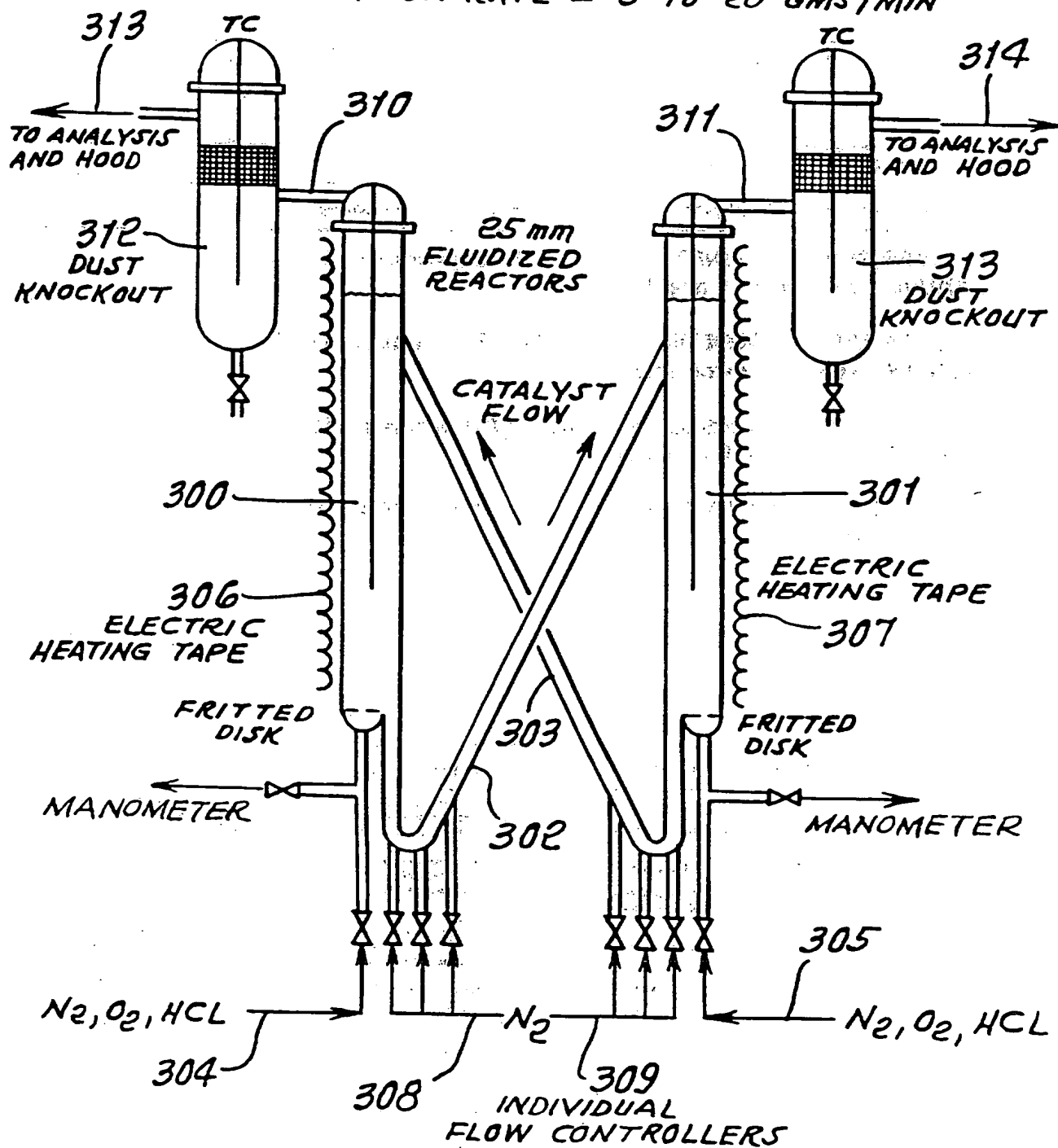
<u>Reaction</u>	<u>COP</u>	<u>COP</u>	<u>COP</u>
Temperature C	200	200	200
Nitrogen flow, ml/min	450	450	450
Oxygen flow, ml/min	85	85	85
HCl flow, ml/min	70	70	70
HCl out, ml/min	0	0	0
% HCl Recovery	100	100	100

Reactor 2

Temperature C	400	400	400
Sample Time, Min	30	30	30
HCl flow, ml/min	150	150	150
Oxygen flow, ml/min	75	100	150
Nitrogen flow, ml/min	325	300	250
Chlorine out, Moles	0.11	0.12	0.12
HCl out, Moles	0.091	0.082	0.065
<hr/>			
% Chlorine Recovery	71	75	79
Total Moles of HCl	0.311	0.322	0.305
HCl Out Flow R2, ml/min	68	61	48.5

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BENCH SCALE FLUIDIZED REACTOR  
CIRCULATION RATE = 5 TO 20 GMS/MIN



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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/15637

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 7/04

US CL : 423/502,507

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/502,507493,604

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
none

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,959,202 A (MINET ET AL) 25 September 1990 (25/09/90), see claim 1 and Fig. 1	
A	US 2,448,255 A (BENEDICTIS ET AL) 31 August 1948 (31/08/48), see entire document.	
A	US 4,119,705 A (RIEGEL ET AL) 10 October 1978 (10/10/78), see claim 1 and the Fig.	
A	US 3,332,742 A (METAIZEAU) 25 July 1967 (25/07/67), see entire document.	

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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* O* document referring to an oral disclosure, use, exhibition or other means		
* P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

23 DECEMBER 1996

Date of mailing of the international search report

04 FEB 1997

Name and mailing address of the ISA/US  
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